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Ni/Silica catalyzed acetylation of phenols and naphthols: An eco-friendly approach

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Abstract A method for 10% Ni/SiO_2 catalyst is developed for acetylation of phenol, substituted phenols, naphthols, substituted alcohols under mild liquid phase conditions affording aromatic esters with maximum conversions of 50–80% and 100% selectivity. The catalyst showed remarkable reusability for up to 4 cycles. This methodology is eco-friendly, economic with Ni/SiO_2 catalysts exhibiting no loss of activity the first report for acetylation of substituted phenols to esters with 10% Ni/SiO_2 catalyst.

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1. Introduction

Acetylation is one of the fundamental reactions in organic chemistry and can be carried out by a wide variety of reagents (Ogliaruso et al., 1979). Acyl groups play an important role in the chemistry of bio-molecules (Simmonds, 1992), they are fragments of important natural products, such as peptides (Bodanszky, 1993) or modified peptide bond iso-esters (Magrath and Abeles, 1992) and also they serve as protecting groups (Greene and Wuts, 1991). *Ortho*-Hydroxy-aryl ketones, as a variety of compounds with the acyl group, are also important synthetic intermediates in the synthesis of biologically active compounds such as chalcones, flavanones, naphthoquinones and pesticides. The acylation of alcohols, phenols, thiols, and amines is very important in various organic transformations, especially in the synthesis of natural compounds and polyfunctional molecules such as nucleosides, carbohydrates, and steroids (Crouse et al., 1981).

A number of lewis acids such as TMSCl (Roux and Dubac, 1996), MoO_2Cl_2 (Chen et al., 2005), $ErCl_3$ (Dalpozzo et al., 2007), $RuCl_3$ (De, 2004), $ZrOCl_2$ (Ghosh et al., 2005), $Zn(ClO_4)_2$ (Bartoli et al., 2003), $TiCl_4$ + $AgClO_4$ (Miyashita et al., 1993), $Cu(OTf)_2$ ($TfCF_3SO_2$) (Tai et al., 2003), $Er(OTf)_3$ (Procopio et al., 2004), $Al(OTf)_3$ (Kamal et al., 2007), $TiCl_3(OTf)$ (Firouzabadi et al., 2008), $Ce(OTf)_3$ (Bartoli et al., 2004), SnIV(tpp)$(OTf)_2$ (tpp = tetra phenylporphyrin) (Moghadam et al., 2004), $Sc(NTf)_3$ (Ishihara et al., 1996a,b), have been reported to show catalytic activity toward the acetylation of alcohols with acid anhydride.

Development of regio-selective reactions in organic compounds is fundamental and important viz. 2-Acylation reactions of phenol and naphthol derivatives that provide useful

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synthetic methods for the preparation of 2-hydroxy phenyl or 2-hydroxy naphthyl ketone derivatives (Procopio et al., 2004). Chakraborti et al. also reported a number of good catalytic systems for the acetylation/acylation reactions (Chakraborti and Gulhane, 2003a,b,c, 2004; Chakraborti et al., 2003a,b, 2004; Chakraborti and Shivani, 2006; Shivani et al., 2007). Particularly, $Sc(OTf)_3$ (Ishihara et al., 1996a,b), a commercially available and moisture-stable lewis acid, is extremely active for this reaction. Unfortunately, due to the high price of scandium salts and its intolerance toward various functional groups, $Sc(OTf)_3$ is limited in application. TMSOTf is another catalyst for acylation of alcohols and phenols (Procopiou et al., 1998). In order to overcome these limitations with lewis acids it is well known that heterogeneous catalysts have advantages over homogeneous catalysts, the recovery of catalysts, easy means of separation, ecofriendly, economic, and reusability.

The aim of this paper is to present the results of acetylation of a series of alcohols viz. 1-naphthol, 2-naphthol, substituted phenols like 2,4 dimethyl phenol and 2,4,6-trimethyl phenols etc. using acetic anhydride as acetylating agent with Ni supported silica catalysts. We also investigated the catalytic activity and various ratios of catalysts 2%, 5% and 10% Ni/SiO_2. The reactions are performed under mild reflux conditions with acetonitrile as solvent.

2. Experimental

2.1. Materials

Acetic anhydride, dichloromethane, nickel nitrate hexa hydrate, ethyl acetate (BDH Chemicals, England), silica gel (ICN Pharamacitical Gmbh, Germany), sodium sulfate anhydrous (Fluka Chemika), phenol (Merck, India), hexanol (Winlab, UK),1-naphthol (Riedel-de Haen, Germany), 2-naphthol (Hopkin &Williams, England), 2,4,6-trimethyl phenol, 3,4-dimethyl phenol (Fluka AG Switzerland) were used as received.

2.2. Preparation of Ni/SiO_2 catalysts

The catalyst was prepared by the impregnation method by dissolving nickel nitrate hexa hydrate (2.5107 g) in distilled water (20.0 mL) and adding it to silica gel (5.0 g) and stirring for 2 h using a magnetic stirrer at room temperature (20 ± 1 °C) and ageing at room temperature overnight. The excess water is removed by heating the mixture on water bath and using a rota-vapor under vacuum to evaporate the water. The catalyst material is dried in an oven at 100–120 °C for 12 h (Rahman et al., 2008).

2.3. Typical reaction procedure

1-Naphthol (2.0 mmol) with 10.0 mL acetonitrile solvent and addition of catalyst (500 mg) followed with slow addition of acetic anhydride 1.5 mmol at room temperature was added in 5 min and the reaction mixture is refluxed continuously until starting material is consumed. The reaction progress is monitored by TLC. The reaction mixture is quenched with de-ionized water and extracted with ethyl acetate. The organic layer is dried on sodium sulfate and the solvent is evaporated on rota-vapor to give crude product of 1-naphthol which is then subjected to column chromatography to afford pure 1-naphthyl acetate product. The final product is characterized by ^1H and ^{13}C NMR (400 MHz Bruker Instrument). GC–MS samples were run on Agilent 6890 GC/5973, MS Column: J&W HP5-MS. GC results were characterized on GC System 6820, Agilent Technologies equipped with flame ionization detection (FID) and a carbovax OVI capillary column and compared with standard sample.

3. Results and discussion

3.1. Characterization of 10% Ni/SiO_2 by BET, XRD, and IR

As reported earlier (Rahman and Jonnalagadda, 2008, 2009), the specific area, i.e., the BET surface area of the catalysts is 180 mg^{-1}. The surface reaction may have caused the decrease of available surface area of the support, probably by uneven distribution of Ni particles on the silica surface. The hydrothermal treatment results in a surface modification, which affects the support surface area. It could be inferred from the increasing specific surface area with time and by the OH stretching band in IR however after 90 h of treatment the BET area decays. When time is increased for hydrothermal treatment, the OH bands show a maximum at 46 h. After that a degradation process can be assumed due to a decrease in the BET area and a starting crystallization process as can be seen by XRD.

IR spectra of 10% Ni/SiO_2 showed a band at 1100 cm^{-1} (asymmetrical Si–O–Si) very perceptive to the formation of silicates and strong intense absorption band between 1078 and 1050 cm^{-1}, showing the presence of Si–O–Ni bonds. Further, upon hydrothermal treatment of catalysts for 46 h, the observed degradation process can be assumed due to a decrease in the BET area. Apart from these hydrothermal treatment at 96 h shows OH stretching vibrations by IR. (Rahman and Jonnalagadda, 2008, 2009) reported the broad band at 3500–3680 cm^{-1} is due to hydrogen bridge bonds.

3.2. Comparative studies of 2%, 5% and 10% Ni/SiO_2 catalysts

10% Ni/SiO_2 gave encouraging results, and further investigated with 2% and 5% Ni/SiO_2 catalysts. The catalyst for acetylation of alcohols by 2% and 5% Ni/SiO_2 resulted in 35% and 55% conversion with 100% selectivity retained which is due to Ni species uneven distribution on silica surface, which have contributed to inactivity of the catalysts. Nickel silicates with layered structure, are well known as polysilicates, hydro silicates, or surface silicates. The authors showed more interest in preparing 10% Ni/SiO_2 catalyst by a simple impregnation method. The fine amorphous powder of 10% Ni/SiO_2 was obtained, which shows that Ni particles are well distributed over the silica surface and confirmed by the XRD characterization technique. Selective acylation of alcohols is an important transformation from industry point of view (Rahman and Jonnalagadda, 2009). 10% Ni/SiO_2 1-naphthol was acylated to 1-naphthyl ester in acetic anhydride. The controlled acylations of 2-naphthol to its ester product are with excellent conversion and selectivity (Rahman et al., 2008). When acetic anhydride is added to nickel silica catalysts at room temperature acylinium ion is generated on the Ni silica surface due to lewis acid

Table 1 Acetylation of aliphatic/aromatic alcohols with 10% Ni/SiO_2.

S. no.	Substrate	Time (h)	Amount of catalysts (mg)	Temp. (°C)	Product	Conv. (%)
1	1-Naphthol	4	500	65	1-Naphthyl acetate	90
2	2-Naphthol	4	500	65	2-Naphthyl acetate	100
3	Phenol	4	500	65	Phenyl acetate	90
4	Hexanol	4	500	65	Hexyl acetate	65
5	3,4-Dimethyl phenol	10	720	120	3,4-Dimethylphenyl acetate	80
6	2,4,6-Trimethyl phenol	10	720	120	2,4,6-Dimethylphenyl acetate	75

character which enhances the rate of reaction leading to the final product. Generally it proceeds via an acyl-oxygen cleavage bimolecular mechanism. According to the mechanism, the density of the acid active sites i.e., the hydroxyl group present on silica surface, facilitates the formation of Ni-acylium ion, which rapidly leads to the product formation.

This indicates that Ni species adhered to the silica surface is superactive catalysts for acylation of alcohols, phenols, naphthols, substituted phenols. Jonnaagadda et al. reported knoevenegal condensation which is achieved with catalytic amounts of nickel silica catalysts (Rahman and Jonnalagadda, 2008, 2009). These catalytic reactions were conducted in liquid phase conditions. The 10% Ni/SiO_2 catalysts emerged to be highly active catalysts for knoevenegal reactions. All the acylation reactions gave 100% selectivity but the conversions varied depending on the substituted alcohols due to ortho, meta, para directing groups, which block the active sites of the catalysts. All the Ni-supported catalysts were characterized by XRD, IR, BET (Rahman and Jonnalagadda, 2008, 2009). The characterized catalyst showed best results compared with the literature reported catalysts (Rahman et al., 2008). A model reaction was tested for leaching of Ni metal from 10% Ni/SiO_2 catalyst the filtrate was again subjected for acetylation reaction with model substrate under the same conditions it was observed that the reaction did not occur and the Ni metal was intact on the surface of silica support which is confirmed by IR studies which confirm that nickel silica is heterogeneous catalysts (Rahman and Jonnalagadda, 2009).

The catalytic tests indicated that supported Ni/SiO_2 catalysts were indeed very active in O-acylation at room temperature (Table 1). The data presented in Table 1 indicate that linear saturated alcohols were quantitatively transformed at a lower conversion than 3,4-dimethyl phenol and 2,4,6-trimethyl phenol. In all these cases, the nice smelling esters were the only identified products and, in the absence of the catalyst, the reaction was very slow compared to the catalyzed one. The 10% Ni/SiO_2 supported catalysts were also very active in the acetylation of aromatic phenols and naphthols at room temperature. The formation of O-acetylated compounds was also detected in the absence of the catalysts, but no C-acylated compounds were identified under these conditions. Thus, at room temperature, there was no conversion observed for 4 h then it was refluxed for 1-naphthol, the conversion to the O-acetylated product was near half in the presence of the catalysts, and about 90% conversion for 1-naphthol. The introduction of the catalysts enhanced the reaction rate and after the same reaction time, the conversions are presented in Table 1 2-Naphthol 100% conversion, 1-naphthol 90% conversion, 1-hexanol 65% and phenol 90% conversion. While 2,4,6-trimethyl phenol and 3,4-dimethyl phenol under similar conditions resulted in recovery of starting material and authors increased the catalytic amount from 500 mg to 750 mg and increase of temperature to 100 °C for 10 h duration which lead to 75% conversion for 2,4,6-trimethyl phenol and 80% conversion for 3,4-dimethyl phenol the increase in temperature and catalytic amount played a key role for these 2 substrates due to its substituents present in the ortho position, which have blocked the active sites of the catalysts.

3.3. Catalyst recovery investigation

To test the reusability of the catalysts and reproducibility of catalytic performance, 10% Ni/SiO_2 was subject to cycles of acetylation reaction of 1-naphthol with acetic anhydride. It was found that the change in product yield was minimal in a test of 4 cycles, indicating that the catalyst is stable and suitable for reuse.

4. Conclusions

Acetylation of phenol, substituted phenols, naphthols and substituted alcohols were investigated with 10% Ni/SiO_2 under mild liquid phase conditions affording aromatic esters with maximum conversions of 50–80% and 100% selectivity. The catalyst showed remarkable reusability for 4 cycles with stability being retained, whereas 2% and 5% Ni/SiO_2 catalysts did not exhibit any activity. The XRD, BET and IR characterization of 10% Ni/SiO_2 catalysts prove that the catalyst is active for acetylation reactions. This methodology is eco-friendly, economic with 10% Ni/SiO_2 catalysts exhibiting no loss of activity.

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References

Bartoli, G., Bosco, M., Dalpozzo, R., Marcantoni, E., Massaccesi, M., Sambri, L., 2003. Eur. J. Org. Chem. 2003, 4611–4617.
Bartoli, G., Dalpozzo, R., Nino, A.D., Maiuolo, L., Nardi, M., Procopio, A., Tagarelli, A., 2004. Green Chem. 6, 191–192.
Bodanszky, M., 1993. Peptide Chemistry. Springer, Berlin.
Chakraborti, A.K., Gulhane, R., 2004. Synlett 2004, 627–630.
Chakraborti, A.K., Gulhane, R., 2003a. Tetrahedron Lett. 44, 6749–6753.
Chakraborti, A.K., Shivani, R., 2006. J. Org. Chem. 71, 5785–5788.
Chakraborti, A.K., Gulhane, R., 2003b. Chem. Commun., 1896–1897.

Chakraborti, A.K., Gulhane, R., 2003c. Tetrahedron Lett. 44, 3521–3525.
Chakraborti, A.K., Gulhane, R., Shivani, R., 2003a. Synlett 203, 1805–1808.
Chakraborti, A.K., Gulhane, R., Shivani, R., 2004. Synthesis, 111–115.
Chakraborti, A.K., Sharma, L., Gulhane, R., Shivani, R., 2003b. Tetrahedron 59, 7661–7668.
Chen, C.T., Kuo, J.H., Pawar, V.D., Munot, Y.S., Weng, S.S., Ku, C.H., Liu, C.Y., 2005. J. Org. Chem. 70, 1188–1197.
Crouse, D.J., Hulbut, S.L., Wheeler, D.M.S., 1981. J. Org. Chem. 46, 374–378.
Dalpozzo, R., Nino, A.D., Maiuolo, L., Oliverio, M., Procopio, A., Russo, B., Tocci, A., 2007. Aust. J. Chem. 60, 75–79.
De, S.K., 2004. Tetrahedron Lett. 45, 2919–2922.
Firouzabadi, H., Iranpoor, N., Farahi, S., 2008. J. Mol. Catal. A 289, 61–68.
Greene, T.W., Wuts, P.G.M., 1991. Protective Groups in Organic Synthesis. John Wiley & Sons Inc., New York.
Ghosh, R., Maiti, S., Chakraborty, A., 2005. Tetrahedron Lett. 45, 147–151.
Ishihara, K., Kubota, M., Yamamoto, H., 1996a. Synlett 1996, 265–266.
Ishihara, K., Kubota, M., Kurihara, H., Yamamoto, H., 1996b. J. Org. Chem. 61, 4560–4567.
Kamal, A., Khan, M.N.A., Reddy, K.S., Srikanth, Y.V.V., Krishnaji, T., 2007. Tetrahedron Lett. 48, 3813–3818.
Magrath, J., Abeles, R.H., 1992. J. Med. Chem. 35, 4279–4283.
Miyashita, M., Shina, I., Miyoshi, S., Mukaiyama, T., 1993. Bull. Chem. Soc. Jpn. 66, 1516–1527.
Moghadam, M., Tangestaninejad, S., Mirkhani, V., Mohammadpour-Baltork, I., Shaibani, R., 2004. J. Mol. Catal. A 219, 73–78.
Ogliaruso, M.A., Wolfe, J.F., Patai, S. (Eds.), 1979. In the Chemistry of Acid Derivatives: Supplement B, Part 1. Interscience, Chichester, pp. 267–490.
Procopio, A., Dalpozzo, R., Nino, A.D., Maiuolo, L., Russo, B., Sindona, G., 2004. Adv. Synth. Catal. 346, 1465–1470.
Procopiou, P.A., Baugh, S.P.D., Flack, S.S., Inglis, G.G.A., 1998. J. Org. Chem. 63, 2342–2347.
Rahman, A., Jonnalagadda, S.B., 2008. Cat. Lett. 123, 264–268.
Rahman, A., Jonnalagadda, S.B., 2009. J. Mol. Cat. A 299, 98–101.
Rahman, A., Pullabhotla, V.S.R.R., Jonnalagadda, S.B., 2008. Cat. Commun. 9, 2417–2421.
Roux, C.L., Dubac, J., 1996. Organometallics 15, 4646–4648.
Simmonds, R.J., 1992. Chemistry of Biomolecules: An Introduction. The Royal Society of Chemistry, Cambridge.
Shivani, R., Gulhane, R., Chakraborti, A.K., 2007. J. Mol. Catal. A 264, 208–213.
Tai, C.A., Kulkarni, S.S., Hung, S.C., 2003. J. Org. Chem. 68, 8719–8722.